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# Cationic mono and dicarbonyl pincer complexes of rhodium and iridium to assess the donor properties of PC<sub>carbene</sub>P ligands†

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The donor properties of five different PC<sub>carbene</sub>P ligands are assessed by evaluation of the CO stretching frequencies in iridium(i) and rhodium(i) carbonyl cations. The ligands feature dialkyl phosphine units (R = <sup>i</sup>Pr or <sup>t</sup>Bu) linked to the central benzylic carbon by either an *ortho*-phenylene bridge, or a 2,3-benzo[*b*]thiophene linker; in the former, substituent patterns on the phenyl linker are varied. The carbonyl complexes are synthesized from the (PC<sub>carbene</sub>P)M–Cl starting materials via abstraction of the chlorides in the presence of CO gas. In addition to the expected mono carbonyl cations, products with two carbonyl ligands are produced, and for the rhodium example, a novel product in which the second carbonyl ligand adds reversibly across the Rh=C bond to give an η<sup>2</sup> ketene moiety was characterized. The IR data for the complexes shows the 2,3-benzo[*b*]thiophene linked system to be the poorest overall donor, while the phenyl bridged ligands incorporating electron donating dialkyl amino groups *para* to the anchoring carbene are very strongly donating pincer arrays.

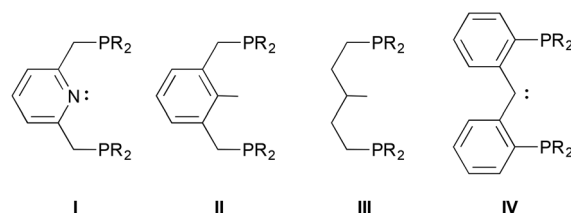
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## Introduction

Pincer ligands are tridentate frameworks that provide a multitude of permutations for supporting complexes of main group elements, transition metals and lanthanides.<sup>1</sup> They are often classified according to the three donor atoms directly involved in chelating the central element; for example, the archetypal ligand I<sup>2</sup> is a “PNP” pincer donor system. For late transition metals,<sup>3,4</sup> flanking phosphorus-based donors comprises a common motif, and when the anchoring element of the framework is also a strong donor, the complexes that result are capable of a variety of bond activations for catalytic applications.<sup>5–7</sup>



PCP pincer ligands have been studied widely,<sup>8</sup> exemplified by one of the first pincer ligand assemblies II,<sup>9</sup> in which the carbon is sp<sup>2</sup> hybridized and a monoanionic X-type donor. A number of PC<sub>sp<sup>3</sup></sub>P ligands,<sup>10</sup> like III,<sup>11</sup> are also known. A third class of PCP pincer ligands incorporate an sp<sup>2</sup> hybridized carbene donor in the anchoring position;<sup>12–14</sup> here the ligands can be formally neutral or dianionic depending on the character of the carbene donor and the metal to which the ligand is bound. For example, the PC<sub>carbene</sub>P ligand system IV<sup>15</sup> behaves in a “Fischer-like” manner when bound to iridium<sup>16</sup> or rhodium(i),<sup>17,18</sup> but in a “Schrock-like” way when supporting nickel(ii)<sup>19</sup> complexes. Indeed, intermediate behaviour along this continuum is observed in the palladium chemistry associated with these ligands.<sup>20,21</sup> The weakly π donating aromatic linking group accounts for this ambiguity and also modulates the reactivity of the carbene motif within the pincer complexes it supports.

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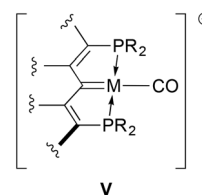
Although the diphenylphosphino version of ligand **IV** was initially reported in the 1990s,<sup>15</sup> the dialkylphosphino examples we recently introduced<sup>16</sup> have been explored more intensively in the past few years,<sup>22–30</sup> in part because of this opportunity for ligand cooperativity involving the carbene moiety<sup>31,32</sup> and also because of the electron richness of the donor ensemble. Indeed, we initially envisioned these ligands as being capable of supporting E–H bond activations (E = N, O) because of their strong donor character.<sup>33,34</sup> However, lacking concrete data that suggest this expectation is rooted in reality, we have endeavoured to garner a measure of their donor character by preparing some carbonyl compounds to establish their place within the pantheon of other electron rich pincer ligands. Herein, we describe the synthesis of cationic mono and dicarbonyl complexes starting from the collection of rhodium and iridium(I) PC<sub>carbene</sub>P chlorido compounds shown in Scheme 1. The trends in the IR stretching frequencies of these complexes are used to assess the relative donor ability of the various PC<sub>carbene</sub>P donor arrays.

## Results and discussion

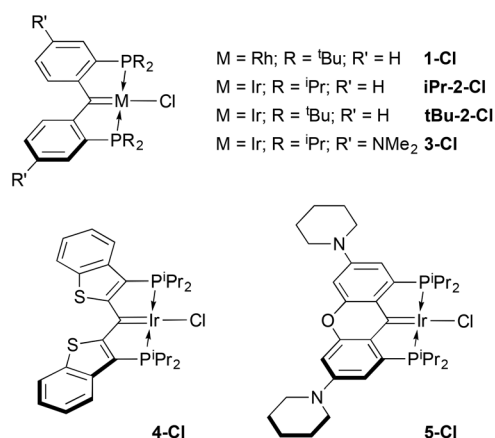
Details concerning the syntheses of the ligands and their rhodium(I) (**1-Cl**<sup>18</sup>) or iridium(I) chloro carbene complexes (**iPr-2-Cl**,<sup>16</sup> **tBu-2-Cl**,<sup>23</sup> **3-Cl**,<sup>35</sup> and **4-Cl**<sup>25</sup>) have been previously published. The xanthene-based ligand variation seen in **5-Cl** is, however, a new ligand/complex. Related to the NMe<sub>2</sub> substituted ligand in **3-Cl**, the oxygen atom linker is designed to planarize and rigidify the ligand framework, improving stability,<sup>35</sup> while retaining the electron donating dialkylamino groups. This ligand was prepared in two steps (54% yield) from the known 1,8-dibromo-3,6-di(piperidin-1-yl)-9H-xanthen-9-one<sup>36</sup> by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyzed reductive silylation of the ketone unit,<sup>37–39</sup> followed by dilithiation with *tert*-butyl lithium and quenching with ClP(*i*Pr)<sub>2</sub>. The resulting prolignand 1,1'-(1,8-bis(diisopropylphosphino)-9H-xanthene-3,6-diyl)dipiperidine was attached to

iridium using [Ir(COE)<sub>2</sub>(μ-Cl)]<sub>2</sub> via a double C–H activation protocol,<sup>16,40</sup> yielding the new complex **5-Cl** as an analytically pure dark brown solid in 75% isolated yield. The carbene carbon resonates at 183.0 ppm (<sup>2</sup>J<sub>CP</sub> = 3.7 Hz) and X-ray quality crystals were obtained via slow evaporation of a pentane solution of the complex. A depiction of the structure is shown in Fig. S17 in the ESI;† the Ir=C distance of 1.921(6) Å is typical for these complexes<sup>16</sup> and reflective of double bond character.

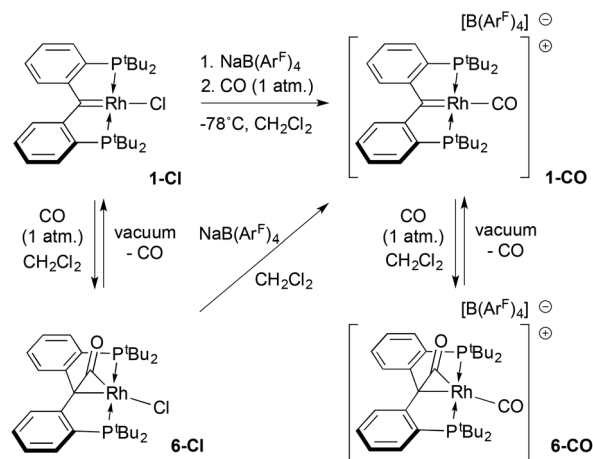
It was envisioned that a compilation of the CO stretching frequencies of carbonyl derivatives of these rhodium and iridium complexes could be used to assess the relative donor abilities of these ligands. Cationic M(I) carbonyl complexes of the form depicted in **V** were therefore targeted. Examples of several of these complexes containing other pincer ligands are available in the literature,<sup>41–49</sup> allowing for comparison with our PC<sub>carbene</sub>P systems; accordingly, protocols towards such compounds starting from the chloro compounds in Scheme 1 were developed. While carbonyl compounds akin to **V** were obtained for all examples, the chemistry is somewhat more complex in that dicarbonyl cations and products arising from reactions of carbon monoxide with the M=C unit of the ligand were also characterized.



We start with a description of the chemistry involving Rh(I) complex **1-Cl**, which is summarized in Scheme 2. A 1:1 mixture of **1-Cl** and sodium tetrakis(3,5-bis-trifluoromethylphenyl) borate (Na[B(Ar<sup>F</sup>)<sub>4</sub>]) was suspended in dichloromethane at –78 °C and exposed to one atmosphere of CO. Upon warming, a rapid colour change from the green colour of



**Scheme 1** Ensemble of PC<sub>carbene</sub>P metal chloro compounds evaluated in this study.



**Scheme 2** CO chemistry of compound **1-Cl**.

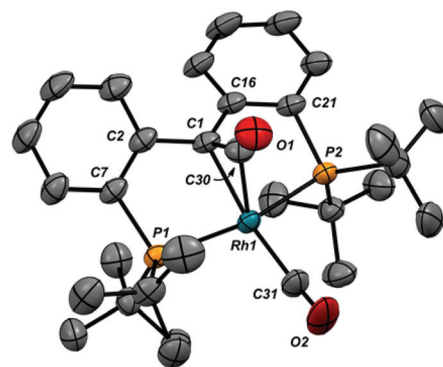


**1-Cl** to deep purple was followed by a slow lightening to pale yellow over the course of  $\approx 30$  minutes. Monitoring the reaction by  $^{31}\text{P}$  NMR spectroscopy showed that an initial product characterized by a doublet at 96.3 ppm ( $^1J_{\text{RhP}} = 140.6$  Hz) converted to the final product (79.0 ppm,  $^1J_{\text{RhP}} = 106.8$  Hz).

The magnitude of the RhP coupling constants in these species imply that the purple intermediate is a Rh(I) complex, while the final product is a Rh(III) derivative.<sup>50</sup> Spectroscopic and structural data identify the latter species as the pale yellow cationic carbonyl complex **6-CO** (Scheme 2) in which a second CO molecule has added to the Rh=C moiety of the ligand to form an  $\eta^2$  ketene ligand. An analogous complex, **6-Cl**, can be prepared by treating **1-Cl** with one atmosphere of CO in the absence of  $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ . In the proton NMR spectra of both **6-CO** and **6-Cl**, the pattern of two virtual triplet resonances for the *tert*-butyl groups on phosphorus reflect the  $C_s$  symmetry of these molecules as opposed to the  $C_{2v}$  symmetry of the starting complex **1-Cl** or the cationic monocarbonyl target **1-CO**. For **6-CO**, the  $^{13}\text{C}$  NMR spectrum exhibits two doublets of triplets at 195.3 ppm ( $^1J_{\text{RhC}} = 22.1$  Hz;  $^2J_{\text{PC}} = 5.3$  Hz), and 190.1 ppm ( $^1J_{\text{RhC}} = 66$  Hz;  $^2J_{\text{PC}} = 12.4$  Hz) for the carbons of the ketene carbonyl moiety and the terminal carbonyl, respectively. This assignment is based on an observed carbon shift of 212.3 ppm ( $^1J_{\text{RhC}} = 26.5$  Hz;  $^2J_{\text{PC}} = 5.8$  Hz) for the ketene CO carbon in **6-Cl**. In **6-CO**, the resonance for the former carbene carbon of the  $\text{PC}_{\text{carbene}}\text{P}$  was shifted significantly upfield, appearing as a doublet of triplets ( $^1J_{\text{RhC}} = 6.7$  Hz;  $^2J_{\text{PC}} = 3.5$  Hz) at 43.2 ppm. In the IR spectrum, two  $\nu_{\text{CO}}$  stretches at 2050 and 1860  $\text{cm}^{-1}$  were recorded; a band at 1787  $\text{cm}^{-1}$  was observed for **6-Cl**, indicating a C=O formulation for the ketene ligand.

While addition of CO to the Rh=C bond was reversible (see below), release of CO was slow enough at atmospheric pressure to permit growth of crystals of both **6-Cl** and **6-CO** from dichloromethane solutions layered with pentane. The structure of the cation of **6-CO** is shown in Fig. 1, along with selected metrical parameters; the structure of **6-Cl** can be found in Fig. S18 in the ESI.<sup>†</sup> In addition to the terminal CO ligand, the structure confirms the addition of a CO to the Rh=C double bond; the Rh1–C1 distance of 2.105(3) Å is significantly elongated from the 1.900(3) Å Rh–C1 distance found in **1-Cl**.<sup>18</sup> The C1–C30 bond length of 1.442(5) Å is consistent with a  $\text{C}_{\text{sp}^3}\text{--C}_{\text{sp}^2}$  single bond, while the C30–O1 length of 1.171(4) is similar to the C–O bond length of 1.162 Å in  $\text{CO}_2$ .<sup>51</sup>

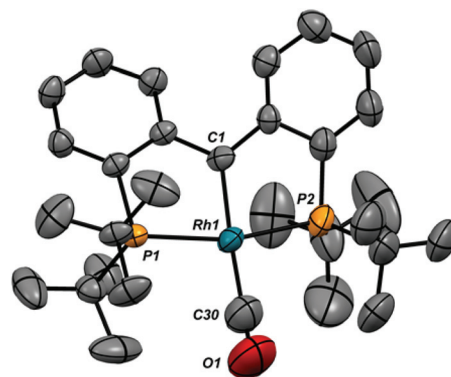
Exposure of compounds **6-Cl** or **6-CO** to high vacuum resulted in loss of CO by reversal of the CO addition to the Rh=C moiety; in the former case, this regenerated carbene chloride **1-Cl**, while in the latter this allowed for isolation of the targeted cationic carbonyl complex of the  $\text{PC}_{\text{carbene}}\text{P}$  ligand as a purple solid. NMR spectroscopic data for samples of **1-CO** isolated in this way indicate that this was the intermediate observed when the reaction of **1-Cl**/ $\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$  mixtures with CO was monitored spectroscopically. The  $\nu_{\text{CO}}$  stretching frequency for the carbonyl ligand was measured to be 2026  $\text{cm}^{-1}$ , 24 wavenumbers below that recorded for the terminal CO ligand in **6-CO**. As indicated in Scheme 1, analytically pure samples of **1-CO** were best prepared from isolated **6-Cl** and



**Fig. 1** X-ray structure of the cation in **6-CO** (thermal ellipsoids drawn to 50% probability level). Hydrogen atoms and the  $\text{B}(\text{Ar}^{\text{F}})_4$  counteranion are omitted for clarity. Selected bond distances (Å): Rh1–C1, 2.105(3); Rh1–C30, 1.992(4); Rh1–C31, 1.929(4); Rh1–P1, 2.3537(8); Rh1–P2, 2.3541(9); C1–C30, 1.442(5); C30–O1, 1.171(5); C31–O2, 1.124(5). Selected bond angles ( $^\circ$ ): P1–Rh1–P2, 161.87(3); C1–Rh1–C31, 160.22(18); C1–Rh1–C30, 41.10(14); C1–C30–Rh1, 73.6(2); C1–C30–O1, 149.6(4); O1–C30–Rh1, 136.5(3); C30–C1–Rh1, 65.26(18); C2–C1–C16, 121.7(3).

$\text{Na}[\text{B}(\text{Ar}^{\text{F}})_4]$ ; this observation suggests that **6-Cl** is an intermediate on the way to formation of **1-CO**, which gets converted in a slower step to **6-CO** when excess carbon monoxide is present.

Ion pair **1-CO** was also characterized crystallographically; the structure of the cation, along with selected metrical parameters, is given in Fig. 2. The structure represents a fairly typical Rh(I) square planar complex, and the Rh1–C1 distance of 1.944(10) Å, while slightly elongated from that in **1-Cl**, is still clearly indicative of restoration of the Rh=C bond.<sup>48</sup> Addition of an excess of CO to solutions of **1-CO** regenerates **6-CO** quantitatively over the course of roughly 30 minutes. The addition of carbon monoxide to a metal carbene with C–C bond formation to give a ketene is a model reaction for a



**Fig. 2** X-ray structure of the cation in **1-CO** (thermal ellipsoids drawn to 50% probability level). Hydrogen atoms and the  $\text{B}(\text{Ar}^{\text{F}})_4$  counteranion are omitted for clarity. Selected bond distances (Å): Rh1–C1, 1.944(10); Rh1–C30, 1.940(19); Rh1–P1, 2.311(3); Rh1–P2, 2.324(3); C30–O1, 1.15(2). Selected bond angles ( $^\circ$ ): P1–Rh1–P2, 164.03(11); C1–Rh1–C30, 165.3(7); C1–Rh1–P1, 83.5(3); C1–Rh1–P2, 81.5(3); P1–Rh1–C30, 95.5(6); P2–Rh1–C30, 100.4(6).

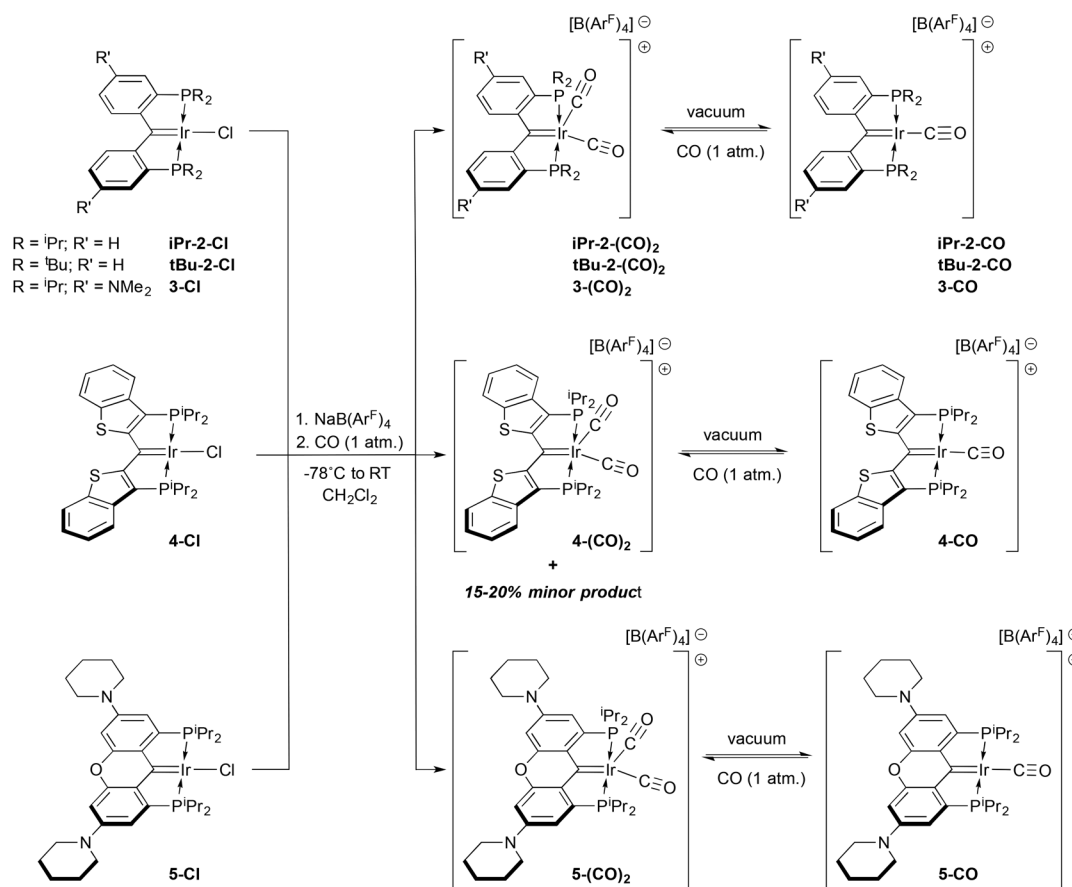


potentially important C–C bond forming mechanism in the Fischer–Tropsch process.<sup>52,53</sup> While several model systems exist in the literature, examples that exhibit facile reversibility are rare.<sup>54,55</sup>

Analogous reactions using the iridium complexes **2–5-Cl**, lead to somewhat different outcomes compared to that seen for the rhodium carbene chloride **1-Cl** (Scheme 3). Equimolar suspensions of the iridium starting material and the chloride abstracting agent Na[B(Ar<sup>F</sup>)<sub>4</sub>] in CH<sub>2</sub>Cl<sub>2</sub> did not visibly react until an atmosphere of CO was admitted into the vessel, whereupon a rapid color change from the generally dark green colors of the carbene chlorides to red or purple solutions were observed. Concentration of these solutions by removal of the solvent *in vacuo*, while keeping the vessel cooled below room temperature, allowed for isolation of the dicarbonyl cations **N-(CO)<sub>2</sub>** shown in Scheme 3 in moderate to excellent yields (62–99%) rather than the expected monocarbonyl cations. In only one case, that of **4-Cl**, was a second product observed in these reactions. This minor species was formed in 15–20% yield but could be minimized to less than 10% by using 1.5 equivalents of Na[B(Ar<sup>F</sup>)<sub>4</sub>] and gently heating the **4-Cl**/Na[B(Ar<sup>F</sup>)<sub>4</sub>] mixture prior to addition of CO. We speculate that this minor species, which is manifested by a signal at 29.6 ppm in the <sup>31</sup>P NMR spectrum, is analogous to the

rhodium ketene carbonyl cation **6-CO** described above. This is supported by its apparent C<sub>s</sub> symmetry in the <sup>1</sup>H NMR spectrum, but attempts to prepare this species cleanly met with failure. Furthermore, reactions of any of the iridium carbene chlorides **N-Cl** (N = 1–5) with CO in the absence of Na[B(Ar<sup>F</sup>)<sub>4</sub>] were much more complex than the reaction of **1-Cl** with CO to form **6-CO** (Scheme 2). It thus appears that addition of CO to the Ir=C bond in these complexes is not as facile as addition to the Rh=C bonds in **1-Cl** or **1-CO**; rather, more conventional carbonyl complexes such as the observed dicarbonyl cations are the preferred products of CO addition to the iridium mono-carbonyl cations **2–5-CO** and the carbene chlorides **2–5-Cl**.

The monocarbonyl cations could be prepared *via* removal of the solvent *in vacuo* from solutions of the dicarbonyl complexes with heating briefly to high temperatures using a heat gun. In some instances, this would need to be repeated by addition of more CH<sub>2</sub>Cl<sub>2</sub> solvent and further heating under dynamic vacuum to ensure sufficient conversion to the monocarbonyl products **N-CO**. Alternatively, in some cases methods that limited the time of exposure of mixtures of **N-Cl** and Na[B(Ar<sup>F</sup>)<sub>4</sub>] to excess CO were the preferred routes to the monocarbonyl cations. The interconversion of these species was monitored *via* <sup>31</sup>P NMR spectroscopy, since the color changes were not distinct enough to allow for visual confirmation of



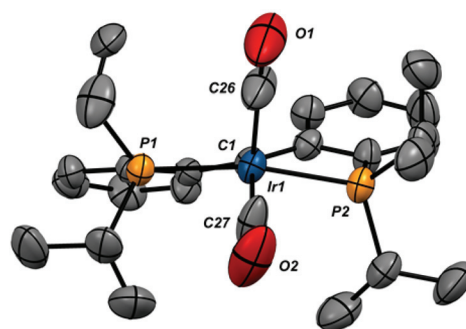
**Scheme 3** Synthesis iridium dicarbonyl cations and monocarbonyl cations.



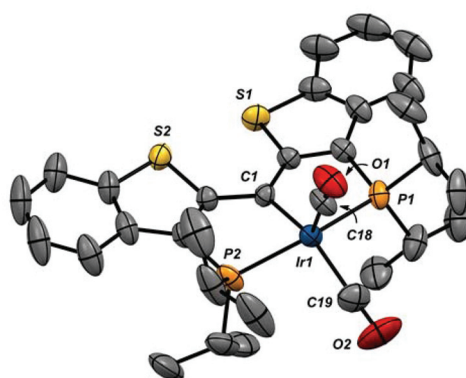
complete reaction. Because of this tendency towards dicarbonyl complexes, it was not always possible to obtain samples of monocarbonyl cations that were analytically pure. Nonetheless, purities of >95% were possible in all cases and the spectroscopic data obtained for each of the monocarbonyl cations reported here is completely consistent with their formulation as depicted in Scheme 3.

All dicarbonyl and monocarbonyl cations were characterized by IR and multinuclear NMR spectroscopies, see Table 1 for selected spectroscopic data. The IR data will be discussed below. In the  $^{31}\text{P}$  NMR spectra, the dicarbonyl compounds exhibited resonances upfield by 7–15 ppm in comparison to those observed for the monocarbonyl cations. Characteristic low field resonances for the carbene carbon were observed and a similar trend towards more upfield-shifted resonances for the dicarbonyl derivatives in comparison to the monocarbonyl analogues was also noted here. Less variation in the chemical shift for the carbonyl carbons was seen, but again the observed shifts for the dicarbonyl species were upfield of the range seen for the monocarbonyl compounds. In the former complexes, the two carbonyl ligands are likely made equivalent due to a fast exchange process that could not be frozen out at lower temperatures. In light of the lability of the second CO ligand, it is reasonable to propose a dissociative mechanism for this exchange, but fluxionality through a pseudo rotation is also feasible. The mechanistic nature of this exchange process was not probed in further detail.

The X-ray structures of compounds **2-iPr-(CO)<sub>2</sub>**, **4-(CO)<sub>2</sub>** and **3-CO** were determined *via* single crystal X-ray diffraction; the structures of the cations of these ion pairs are shown in Fig. 3–5, respectively, along with selected metrical data. In the dicarbonyl cations **2-iPr-(CO)<sub>2</sub>** and **4-(CO)<sub>2</sub>**, the iridium center is closer to a square pyramidal geometry than trigonal bipyramidal, as defined by their low  $\tau$  values<sup>56</sup> (0.22 for **2-iPr-(CO)<sub>2</sub>** and 0.19 for **4-(CO)<sub>2</sub>**). Nonetheless, the equatorial carbonyl ligand in these structures dips below the basal plane; for **2-iPr-(CO)<sub>2</sub>** the C1–Ir1–C27 angle is 146.3(4)° while for **4-(CO)<sub>2</sub>**



**Fig. 3** X-ray structure of the cation in **2-iPr-(CO)<sub>2</sub>** (thermal ellipsoids drawn to 50% probability level). Hydrogen atoms and the  $\text{B}(\text{Ar}^{\text{F}})_4$  counteranion are omitted for clarity. Selected bond distances (Å): Ir1–C1, 1.967(8); Ir1–C26, 1.894(10); Ir1–C27, 1.932(9); Ir1–P1, 2.3325(18); Ir1–P2, 2.328(2); C26–O1, 1.128(11); C27–O2, 1.121(10). Selected bond angles (°): P1–Ir1–P2, 159.59(8); C1–Ir1–C26, 117.8(4); C1–Ir1–C27, 146.3(4); C26–Ir1–C27, 95.8(5); C1–Ir1–P1, 82.1(2); C1–Ir1–P2, 81.5(2); P1–Ir1–C26, 98.7(3); P2–Ir1–C26, 99.6(3); P1–Ir1–C27, 93.9(3); P2–Ir1–C27, 93.1(3).



**Fig. 4** X-ray structure of the cation in **4-(CO)<sub>2</sub>** (thermal ellipsoids drawn to 50% probability level). Hydrogen atoms and the  $\text{B}(\text{Ar}^{\text{F}})_4$  counteranion are omitted for clarity. Selected bond distances (Å): Ir1–C1, 1.996(6); Ir1–C18, 1.914(7); Ir1–C19, 1.938(8); Ir1–P1, 2.3396(17); Ir1–P2, 2.3401(18); C18–O1, 1.121(8); C19–O2, 1.115(10). Selected bond angles (°): P1–Ir1–P2, 160.98(6); C1–Ir1–C18, 115.4(3); C1–Ir1–C19, 149.8(3); C18–Ir1–C19, 94.8(3); C1–Ir1–P1, 82.53(17); C1–Ir1–P2, 82.44(18); P1–Ir1–C18, 98.4(2); P2–Ir1–C18, 98.6(2); P1–Ir1–C19, 93.0(3); P2–Ir1–C19, 94.2(3).

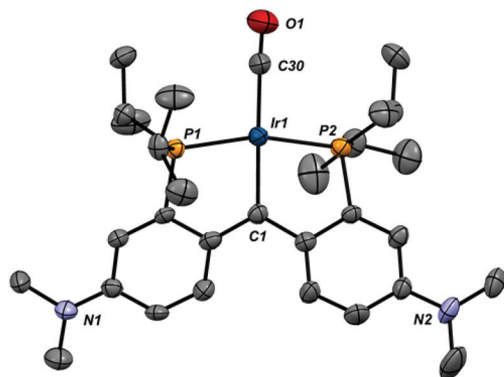
**Table 1** Selected spectroscopic data for iridium di and monocarbonyl cations<sup>a</sup>

Compound	$^{31}\text{P}$ (ppm)	$^{13}\text{C}_{\text{Ir}=\text{C}}$ (ppm)	$^{13}\text{C}_{\text{CO}}$ (ppm)	$\nu_{\text{CO}}$ ( $\text{cm}^{-1}$ )
<b>1-CO</b>	96.3	294.8	200.5	2026
<b>2-iPr-(CO)<sub>2</sub></b>	61.0	233.9	178.2	2050, 2002 (2026) <sup>c</sup>
<b>2-tBu-(CO)<sub>2</sub></b>	81.0	231.8	183.1	2040, 2002 (2021) <sup>c</sup>
<b>3-(CO)<sub>2</sub></b>	58.2	242.4	179.7	2014, 1971 (1993) <sup>c</sup>
<b>4-(CO)<sub>2</sub></b>	47.1	200.1	182.1	2055, 2014 (2035) <sup>c</sup>
<b>5-(CO)<sub>2</sub></b>	62.9	207.4	178.2	2014, 1973 (1994) <sup>c</sup>
<b>2-iPr-CO</b>	68.6	267.8	195.1	2004
<b>2-tBu-CO</b>	82.0	264.2	198.7	2005
<b>3-CO</b>	72.2	260.4	195.9	1963
<b>4-CO</b>	59.6	232.2	188.6	2048 <sup>b</sup>
<b>5-CO</b>	78.6	214.9	196.4	1974

<sup>a</sup> IR spectra acquired on thin films deposited on salt plates. <sup>b</sup> Sample contaminated with 10–15% of **4-(CO)<sub>2</sub>**. <sup>c</sup> Number in parentheses is the average value of the two stretching frequencies.

the C1–Ir1–C19 angle is 149.8(3)°. The Ir–C<sub>carbene</sub> distances in the complexes (**2-iPr-(CO)<sub>2</sub>**, 1.967(8) Å; **4-(CO)<sub>2</sub>**, 1.996(6) Å) are somewhat elongated from the range of 1.899(7)–1.947(4) Å found in neutral, four-coordinate ( $\text{PC}_{\text{carbene}}\text{P}$ )IrX complexes.<sup>16,22,23,26,35</sup> The Ir–C<sub>carbonyl</sub> bond lengths are shorter than the Ir–C1 distances, with the bonds to the apical carbonyl carbons shorter than those to the basal carbonyl carbons by 0.038 Å in **2-iPr-(CO)<sub>2</sub>** and 0.024 Å in **4-(CO)<sub>2</sub>**. The structure of the four coordinate monocarbonyl cation **3-CO** is a distorted square planar geometry with a rather long Ir1–C1 distance of 2.038(9) Å, outside the range previously observed.





**Fig. 5** X-ray structure of the cation in **3-CO** (thermal ellipsoids drawn to 50% probability level). Hydrogen atoms and the  $B(\text{Ar}^{\text{F}})_4$  counteranion are omitted for clarity. Selected bond distances (Å): Ir1–C1, 2.038(9); Ir1–C30, 1.915(10); Ir1–P1, 2.285(2); Ir1–P2, 2.292(2); C30–O1, 1.117(12). Selected bond angles (°): P1–Ir1–P2, 164.25(8); C1–Ir1–C30, 178.0(4); C1–Ir1–P1, 82.5(2); C1–Ir1–P2, 81.7(2); P1–Ir1–C30, 98.0(3); P2–Ir1–C30, 97.7(3).

The comparative donor properties of the various ligands employed here can be evaluated by the IR data collected in Table 1. In general, the observed stretching frequencies for the cationic species here are relatively high in comparison to typical neutral iridium(i) carbonyl complexes, with CO stretching frequencies spanning a range of 1963–2048  $\text{cm}^{-1}$  in the monocarbonyl derivatives. In comparison, the value for a related Vaska's complex analogue  $\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2$ ,<sup>57</sup> which also features dialkylarylphosphine donors, exhibits a  $\nu_{\text{CO}}$  of 1938  $\text{cm}^{-1}$  (1960 in a nujol mull, 1950 in THF<sup>58</sup>). The dicarbonyl compounds, as expected, give rise to two  $\nu_{\text{CO}}$  bands, the low energy band in the range 1971–2014  $\text{cm}^{-1}$ , the high energy stretch appearing between 2014 and 2055  $\text{cm}^{-1}$ . The average value is given in italics in Table 1, and is in most cases larger than the stretch for the analogous monocarbonyl derivative by about 20 wavenumbers; nevertheless, the trends within each family of compounds with respect to ligand variation are consistent. That the stretching frequencies of these cationic compounds are larger than comparable neutral Ir(i) compounds is consistent with the expectation that  $\pi$  backbonding will be attenuated in cationic compounds.

Based on these data, the ligand featuring a 2,3-benzo[*b*]thiophene linker in compounds **4** is the poorest overall donor. The parent system, with the simple  $\text{C}_6\text{H}_4$  linker is somewhat more donating, but incorporating *N,N*-dimethylamino groups in the positions *para* to the carbene carbon increases the donor properties of the  $\text{PC}_{\text{carbene}}\text{P}$  ligand significantly. The installation of the rigidifying oxygen atom bridge in the xanthene-based ligand was motivated by a desire to increase the stability of the ligand system,<sup>35</sup> similar to that found for the a 2,3-benzo[*b*]thiophene linked ligand, while retaining the stronger donating character of the *N,N*-dimethylamino adorned ligand in compounds **3**. The IR data shows that the oxygen atom makes this ligand only slightly less donating, and preliminary reaction chemistry indicates that the ligand framework featured in compounds **5** is

not prone to the C–C bond cleavage processes observed in the parent, unbridged systems.<sup>35</sup>

These dialkylamino substituted ligands are comparable or better overall donors than other common pincer systems in the literature. The IR data for several related monocarbonyl complexes containing other pincer ligands is given in Table S1 in the ESI.† The PNP ligands of type **I** (see Introduction), where the R groups on phosphorus are *tert*-butyl<sup>41–43</sup> or iso-propyl,<sup>42</sup> give mono carbonyl cations with comparable stretches of 1962–1970  $\text{cm}^{-1}$  to those observed for compounds **3-CO** and **5-CO**. These PNP contain more electron-rich tris-alkylphosphine donor arms in comparison to the dialkylaryl donors found in the  $\text{PC}_{\text{carbene}}\text{P}$  ligands discussed here. A related PNP system containing phosphinato donor arms is significantly less donating, with a  $\nu_{\text{CO}}$  stretch of 2010  $\text{cm}^{-1}$  found for its monocarbonyl cation.<sup>44</sup> Other systems, including SNS,<sup>42</sup> NNS,<sup>45</sup> and NNN<sup>46,47</sup> pincer complexes are all less donating than the ligands in compounds **3** and **5** by this criterion.

## Conclusions

Assessment of the global donor properties of a given ligand set is important for rationalizing trends in reactivity, catalytic behaviour and structural properties within related families of compounds. The use of IR stretching frequencies of carbonyl ligands in families of compounds is a common way of evaluating the electronic effects of ligand variation. For relatively new ligand families such as the  $\text{PC}_{\text{carbene}}\text{P}$  ligands discussed here, it is therefore important to establish relative donor properties so as to inform future ligand designs and to rationalize observed reaction trends.

A comparison with available literature data shows that these aryl-linked ligands presented here exhibit better or comparable electron donating ability than common donor arrays. Logical trends in overall electron donating ability are observed based on the expectation that  $\text{NMe}_2$  groups placed *para* to the carbene carbon donor should increase electron density at this center by resonance. This suggests that the electronic properties of the ligands can be tuned in a rather sensitive way by varying groups in this position. Linking substituents *ortho* to the carbene carbon also have an effect; these features may be required to maintain ligand integrity,<sup>35</sup> but also offer a further ligand design handle for tuning the overall properties of the ligand. Interestingly, the ligand featuring a 2,3-benzo[*b*]thiophene linker is significantly less donating overall, providing another platform for applications in which less basic ligands would be beneficial.

## Experimental section

### General considerations

For a description of general procedures and the synthesis of the xanthene-based ligand and complex **5-Cl** can be found in the ESI.†



**Synthesis of 1-CO.** To a J. Young NMR tube charged with **1-Cl** (0.017 g, 0.029 mmol),  $\text{CD}_2\text{Cl}_2$  (0.7 mL) was added. The solution was degassed, placed under 1 atm of CO and allowed to mix at room temperature for 10 minutes. An immediate colour change from dark green to a very dark yellow/brown was observed. Following mixing the solution was degassed and placed under 1 atm of argon. To this solution sodium tetrakis-[3,5-trifluoromethyl]phenyl]borate (0.047 g, 0.53 mmol) ( $\text{NaB}(\text{Ar}^{\text{F}})_4$ ) was added. The solution immediately turned dark purple and following mixing for 10 minutes was filtered. The filtrate was collected and solvent was removed *in vacuo*. A dark purple solid was isolated in 89% yield (0.037 g, 0.026 mmol). Complex **1-CO** was also accessed by dissolving **6-CO** with chlorobenzene in a thick walled pressure vessel (25 mL) removing solvent *in vacuo* and heating to 100 °C under dynamic vacuum. The yellow material slowly turned red, then darkened to purple as the complex lost the inserted carbonyl. This procedure was repeated 3 times until mostly the mono carbonyl product remained. Unfortunately, this method leads to incomplete conversion of **6-CO** to **1-CO** and can result in degradation upon excess heating.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.19 (t,  $^3J_{\text{HH}} = 7.3$ , 2H, ArH), 8.08 (m, 2H, ArH), 7.73 (m, 8H, CH-ortho,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 7.59 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 4H, ArH), 7.56 (s, 4H, CH-para,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 7.53 (m, 2H, ArH), 1.57–1.25 (br m, 36H,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  294.8 (dt,  $^1J_{\text{CRh}} = 40.2$  Hz,  $^2J_{\text{CP}} = 3.9$  Hz, Rh=C), 200.5 (dt,  $^1J_{\text{CRh}} = 50.8$  Hz,  $^2J_{\text{CP}} = 11.0$  Hz, Rh-CO), 164.1 (dvt,  $J_{\text{CP}} = 16.2$  Hz,  $^2J_{\text{CRh}} = 2.3$  Hz, ArC) 162.2 (q,  $^1J_{\text{CB}} = 49.8$  Hz, C-B,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 143.1 (dvt,  $J_{\text{CP}} = 13.8$  Hz,  $^2J_{\text{CRh}} = 2.9$  Hz, ArC), 136.7 (vt,  $J_{\text{CP}} = 2.6$  Hz, ArCH), 136.0 (s, ArCH), 135.2 (s, CH-ortho,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 133.3 (s, ArCH), 132.5 (vt,  $J_{\text{CP}} = 6.6$  Hz, ArCH), 129.3 (qq,  $^2J_{\text{CF}} = 31.5$  Hz,  $^4J_{\text{CF}} = 2.7$  Hz, C-CF<sub>3</sub>,  $\text{B}(\text{Ar}^{\text{F}})_4$ ), 124.9 (q,  $^1J_{\text{CF}} = 272.4$  Hz, CF<sub>3</sub>,  $\text{B}(\text{Ar}^{\text{F}})_4$ ), 117.9 (sept,  $^3J_{\text{CF}} = 4.0$ , CH-para,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 37.3 (vt,  $J_{\text{CP}} = 7.9$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 30.7 (vt,  $J_{\text{CP}} = 2.8$  Hz,  $\text{C}(\text{CH}_3)_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR (203 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  96.3 (d,  $J_{\text{PRh}} = 140.6$  Hz).  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -63.8 (s).  $^{11}\text{B}\{^1\text{H}\}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -6.0 (s). IR (AgCl plates)  $\text{cm}^{-1}$ :  $\nu_{\text{CO}}$  2026 (m). Elemental Anal. Calcd (%) for  $\text{C}_{58}\text{H}_{48}\text{BF}_{24}\text{OP}_2\text{Rh}$ : C 51.40, H 3.90; Found: C 51.38, H 3.94.

**Synthesis of iPr-2-(CO)<sub>2</sub>.** To a round bottom flask (25 mL) charged with **iPr-2-Cl** (0.038 g, 0.061 mmol),  $\text{NaB}(\text{Ar}^{\text{F}})_4$  (0.054 g, 0.061 mmol) and a Teflon stirbar, DCM (5 mL) was added *via* vacuum transfer at -78 °C. Following vacuum transfer, the atmosphere was replaced with CO (1 atm) which resulted in an immediate color change from green to red. The solution was stirred for 1 hour, at which point the reaction was filtered. The solvent was removed *in vacuo* from the red filtrate and a red solid was isolated in 73% yield (0.067 g, 0.044 mmol).  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.86 (d,  $^3J_{\text{HH}} = 8.0$  Hz, 2H, ArH), 7.72 (m, 2H, ArH), 7.73 (m, 8H, CH-ortho,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 7.62 (dt,  $^3J_{\text{HH}} = 7.7$ ,  $^3J_{\text{HP}} = 4.0$  Hz, 2H, ArH), 7.57 (s, 4H, CH-para,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 7.44 (t,  $^3J_{\text{HH}} = 7.4$  Hz, 2H, ArH), 2.91 (m, 4H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (m, 24H, -CH(CH<sub>3</sub>)<sub>2</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  233.8 (t,  $^2J_{\text{CP}} = 5.6$  Hz, Ir=C), 178.1 (t,  $^2J_{\text{CP}} = 4.3$  Hz, Ir-CO), 166.4 (vt,  $J_{\text{CP}} = 17.1$  Hz, Ar), 162.2 (q,  $^1J_{\text{CB}} = 49.8$  Hz, C-B,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 135.2 (s, CH-ortho,  $\text{B}(\text{Ar}^{\text{F}})_4$ ,

Ar), 133.9 (vt,  $J_{\text{CP}} = 1.7$  Hz, ArCH), 133.6 (s, ArCH), 133.4 (vt,  $J_{\text{CP}} = 25.9$  Hz, ArC), 129.8 (vt,  $J_{\text{CP}} = 4.0$  Hz, ArCH), 129.3 (qq,  $^2J_{\text{CF}} = 30.2$  Hz,  $^4J_{\text{CF}} = 2.9$  Hz,  $\text{B}(\text{Ar}^{\text{F}})_4$ , C-CF<sub>3</sub>, Ar), 125.5 (vt,  $J_{\text{CP}} = 7.2$  Hz, ArCH), 125.0 (q,  $^1J_{\text{CF}} = 272.2$  Hz,  $\text{B}(\text{Ar}^{\text{F}})_4$ , CF<sub>3</sub>), 117.9 (sept,  $^3J_{\text{CF}} = 4.3$  Hz, CH-para,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 25.9 (vt,  $J_{\text{CP}} = 15.7$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 18.5 (s, -CH(CH<sub>3</sub>)<sub>2</sub>), 17.4 (s, -CH(CH<sub>3</sub>)<sub>2</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  61.9 (s).  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -63.4 (s).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -7.1 (s). IR (NaCl plates)  $\text{cm}^{-1}$ :  $\nu_{\text{CO}}$  2050 (s),  $\nu_{\text{CO}}$  2002 (s). Elemental Anal. Calcd (%) for  $\text{C}_{59}\text{H}_{48}\text{BF}_{24}\text{IrOP}_2$ : C 46.93, H 3.20; Found: C 46.92, H 3.48.

**Synthesis of iPr-2-CO.** To a J. Young NMR tube charged with **2-iPr-Cl** (0.010 g, 0.016 mmol), DCM (0.3 mL) was added. The mixture was degassed and placed under 1 atm of CO at room temperature. An immediate colour change from dark green to deep red was observed. The NMR tube was shaken for 3 seconds to allow mixing and then all volatiles were removed *in vacuo*.  $\text{NaB}(\text{Ar}^{\text{F}})_4$  (0.030 g, 0.034 mmol) and  $\text{CD}_2\text{Cl}_2$  were then added to the vessel. An immediate colour change to black was observed. The mixture was filtered and all volatiles from the filtrate were removed *in vacuo*. A black solid was isolated in 87% yield (0.021 g, 0.014 mmol). Complex **2-iPr-CO** was also accessed by heating **2-iPr-(CO)<sub>2</sub>** under dynamic high vacuum. To a thick walled glass pressure flask (25 mL) charged with **iPr-2-(CO)<sub>2</sub>** (0.041 g, 0.027 mmol), DCM (2 mL) was added. The solvent was carefully removed *in vacuo* to give a fairly uniform layer of red solid on the bottom of the flask. The flask was then heated to 180 °C for 30 minutes under dynamic high vacuum. After this, the solid was reconstituted with DCM (2 mL) and the procedure involving solvent removal as well as heating under vacuum was repeated. This was performed 4 times in total. A black solid was obtained in 60% yield (0.024 g, 0.016 mmol).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.44 (t,  $^3J_{\text{HH}} = 7.4$  Hz, 2H, ArH), 8.02 (d,  $^3J_{\text{HH}} = 7.9$  Hz, 2 H, ArH), 7.72 (m, 8H, CH-ortho,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 7.67 (m, 2H, ArH), 7.56 (s, 4H, CH-para,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 7.44 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2H, ArH), 2.93 (m, 4H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.19 (m, 24H, -CH(CH<sub>3</sub>)<sub>2</sub>).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  267.7 (Ir=C), 195.1 (t,  $^2J_{\text{CP}} = 7.5$  Hz, Ir-CO), 167.2 (vt,  $J_{\text{CP}} = 15.5$  Hz, ArC), 162.2 (q,  $^1J_{\text{CB}} = 49.8$  Hz, C-B,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 141.7 (vt,  $J_{\text{CP}} = 20.4$  Hz, ArC), 135.7 (m, ArCH), 135.6 (s, ArCH), 135.3 (s, CH-ortho,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 135.1 (s, ArCH), 130.9 (vt,  $J_{\text{CP}} = 6.3$  Hz, ArCH), 129.4 (qq,  $^2J_{\text{CF}} = 31.8$  Hz,  $^4J_{\text{CF}} = 2.4$  Hz,  $\text{B}(\text{Ar}^{\text{F}})_4$ , C-CF<sub>3</sub>, Ar), 125.0 (q,  $^1J_{\text{CF}} = 272.6$  Hz,  $\text{B}(\text{Ar}^{\text{F}})_4$ , CF<sub>3</sub>), 117.9 (m, CH-para,  $\text{B}(\text{Ar}^{\text{F}})_4$ , Ar), 25.6 (vt,  $J_{\text{CP}} = 15.3$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 19.8 (s, -CH(CH<sub>3</sub>)<sub>2</sub>), 18.9 (s, -CH(CH<sub>3</sub>)<sub>2</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR (203 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  68.0 (s).  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -63.8 (s).  $^{11}\text{B}\{^1\text{H}\}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -6.0 (s). IR (NaCl plates)  $\text{cm}^{-1}$ :  $\nu_{\text{CO}}$  2004 (s). Elemental Anal. Calcd (%) for  $\text{C}_{58}\text{H}_{48}\text{BF}_{24}\text{IrOP}_2$ : C 47.01, H 3.26; Found: C 47.05, H 3.19.

**Synthesis of tBu-2-(CO)<sub>2</sub>.** To a thick walled glass pressure flask (25 mL) charged with **tBu-2-Cl** (0.035 g, 0.051 mmol) and  $\text{NaB}(\text{Ar}^{\text{F}})_4$  (0.045 g, 0.051 mmol), DCM (5 mL) was added *via* vacuum transfer at -78 °C. Following vacuum transfer, the atmosphere was replaced with CO (1 atm) which resulted in an immediate color change of the solution from green to purple. The solution was stirred for 1 hour, at which point the reaction



was filtered. The solvent was removed *in vacuo* from the purple filtrate and a purple solid was isolated in 62% yield (0.050 g, 0.032 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.88 (dvt,  $^3J_{\text{HH}} = 7.7$ ,  $J_{\text{HP}} = 3.7$  Hz, 2H, ArH), 7.79 (t,  $^3J_{\text{HH}} = 8.7$  Hz, 4H, ArH), 7.76 (m, 8H, CH-*ortho*, B(ArF)<sub>4</sub>, Ar), 7.60 (s, 4H, CH-*para*, B(ArF)<sub>4</sub>, Ar), 7.42 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2H, ArCH), 1.53 (vt,  $J_{\text{HP}} = 7.7$  Hz, 36H, C(CH<sub>3</sub>)<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  231.8 (s, Ir=C), 183.1 (t,  $^2J_{\text{CP}} = 3.4$  Hz, Ir-CO), 166.6 (vt,  $J_{\text{CP}} = 16.1$  Hz, ArC), 162.4 (q,  $^1J_{\text{CB}} = 49.9$  Hz, C-B, B(ArF)<sub>4</sub>, Ar), 135.4 (m, CH-*ortho*, B(ArF)<sub>4</sub>, Ar), 135.3 (s, ArCH), 134.5 (vt,  $J_{\text{CP}} = 22.6$  Hz, ArC), 133.2 (s, ArCH), 129.5 (qq,  $^2J_{\text{CF}} = 31.3$  Hz,  $^4J_{\text{CF}} = 2.9$  Hz, B(ArF)<sub>4</sub>, C-CF<sub>3</sub>, Ar), 129.3 (vt,  $J_{\text{CP}} = 3.4$  Hz, ArCH), 126.2 (vt,  $J_{\text{CP}} = 7.0$  Hz, ArCH), 125.2 (q,  $^1J_{\text{CF}} = 272.4$  Hz, CF<sub>3</sub>, B(ArF)<sub>4</sub>), 118.1 (sept,  $^3J_{\text{CF}} = 4.4$  Hz, CH-*para*, B(ArF)<sub>4</sub>, Ar), 39.3 (vt,  $J_{\text{CP}} = 10.6$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 30.9 (vt,  $J_{\text{CP}} = 2.2$  Hz, C(CH<sub>3</sub>)<sub>3</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  81.4 (s).  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -62.8 (s).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -6.6 (s). IR (NaCl plates)  $\text{cm}^{-1}$ :  $\nu_{\text{CO}}$  2044 (s),  $\nu_{\text{CO}}$  2002 (s). Elemental Anal. Calcd (%) for C<sub>63</sub>H<sub>56</sub>BF<sub>24</sub>O<sub>2</sub>P<sub>2</sub>Ir: C 48.32, H 3.60; Found: C 48.32, H 3.80.

**Synthesis of tBu-2-CO.** Compound tBu-2-(CO)<sub>2</sub> (0.011 g, 0.007 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  in a J. Young NMR tube. The solvent was removed *in vacuo* and the residue was carefully heated with a heat gun until a colour change from purple to black was observed. This process was repeated 9–10 times until full conversion was achieved, as monitored by  $^{31}\text{P}$  NMR. A black solid was obtained in 65% yield (0.007 g, 0.005 mmol).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.46 (m,  $^3J_{\text{HH}} = 7.2$  Hz, 2H, ArH), 7.98 (dvt,  $^3J_{\text{HH}} = 7.6$  Hz,  $J_{\text{HP}} = 3.1$  Hz, 2H, ArH), 7.92 (d,  $^3J_{\text{HH}} = 8.0$  Hz, 2H, ArH), 7.72 (m, 8H, CH-*ortho*, B(ArF)<sub>4</sub>, Ar), 7.55 (s, 4H, CH-*para*, B(ArF)<sub>4</sub>, Ar), 7.41 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2H, ArH), 1.45 (vt,  $J_{\text{HP}} = 7.3$  Hz, 36H, C(CH<sub>3</sub>)<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  264.2 (t,  $^2J_{\text{CP}} = 3.1$  Hz, Ir=C), 198.7 (t,  $^2J_{\text{CP}} = 7.2$  Hz, Ir-CO), 168.0 (vt,  $J_{\text{CP}} = 15.3$  Hz, ArC), 162.2 (q,  $^1J_{\text{CB}} = 49.9$  Hz, C-B, B(ArF)<sub>4</sub>, Ar), 141.7 (vt,  $J_{\text{CP}} = 18.0$  Hz, ArC), 136.9 (s, ArCH), 135.2 (m, CH-*ortho*, B(ArF)<sub>4</sub>, Ar), 135.1 (vt,  $J_{\text{CP}} = 3.2$  Hz, ArCH), 134.5 (s, ArCH), 131.8 (vt,  $J_{\text{CP}} = 6.1$  Hz, ArCH), 129.2 (qq,  $^2J_{\text{CF}} = 31.5$  Hz,  $^4J_{\text{CF}} = 2.8$  Hz, B(ArF)<sub>4</sub>, C-CF<sub>3</sub>, Ar), 125.0 (q,  $^1J_{\text{CF}} = 272.8$  Hz, CF<sub>3</sub>, B(ArF)<sub>4</sub>), 117.9 (sept,  $^3J_{\text{CF}} = 4.0$  Hz, CH-*para*, B(ArF)<sub>4</sub>, Ar), 37.7 (vt,  $J_{\text{CP}} = 10.6$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 30.9 (vt,  $J_{\text{CP}} = 2.6$  Hz, C(CH<sub>3</sub>)<sub>3</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  82.0.  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -63.8.  $^{11}\text{B}\{^1\text{H}\}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -6.1. IR (AgCl plates)  $\text{cm}^{-1}$ :  $\nu_{\text{CO}}$  2008 (s). HRMS (ESI+) for C<sub>30</sub>H<sub>44</sub>IrOP<sub>2</sub>; calculated (M<sup>+</sup>): 675.2491 (100%); Found (M<sup>+</sup>): 675.2473 (100%).

**Synthesis of 3-(CO)<sub>2</sub>.** To a thick walled glass pressure flask (25 mL) charged with 3-Cl (0.035 g, 0.049 mmol), NaB(ArF)<sub>4</sub> (0.048 g, 0.054 mmol) and a Teflon stirbar, DCM (5 mL) was vacuum transferred at -78 °C. Following vacuum transfer, the solution was warmed to room temperature and the atmosphere was replaced with CO (1 atm) which resulted in an immediate colour change from dark green to dark purple. The solution was stirred for ten minutes, at which point the solution was filtered. The solvent was removed *in vacuo* from the purple filtrate and a purple solid was obtained in 79% yield (0.062 g, 0.039 mmol). Compound 3-(CO)<sub>2</sub> was also synthesized by dis-

solving 3-CO (0.005 g, 0.003 mmol) in dichloromethane in a J. Young NMR tube, exposing the solution to 1 atm of CO, mixing for 5 minutes and removing all volatiles *in vacuo* (>99% yield, 0.005 g, 0.003 mmol).  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.73 (m, 8H, CH-*ortho*, B(ArF)<sub>4</sub>, Ar), 7.69 (dm,  $^3J_{\text{HH}} = 9.2$  Hz, 2H, ArH), 7.57 (s, 4H, CH-*para*, B(ArF)<sub>4</sub>, Ar), 6.79 (m, 2H, ArH), 6.66 (dd,  $^4J_{\text{HH}} = 2.7$  Hz,  $^3J_{\text{HH}} = 9.2$  Hz, 2H, ArH), 3.06 (s, 12H, -N(CH<sub>3</sub>)<sub>2</sub>), 2.75 (m, 4H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (m, 24H, -CH(CH<sub>3</sub>)<sub>2</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  242.4 (t,  $^2J_{\text{CP}} = 4.8$  Hz, Ir=C), 179.7 (t,  $^2J_{\text{CP}} = 4.9$  Hz, Ir-CO), 162.2 (q,  $^1J_{\text{CB}} = 49.9$  Hz, C-B, B(ArF)<sub>4</sub>, Ar), 152.5 (vt,  $J_{\text{CP}} = 4.5$  Hz, ArC), 151.8 (vt,  $J_{\text{CP}} = 15.8$  Hz, ArC), 143.8 (vt,  $J_{\text{CP}} = 23.5$  Hz, ArC), 135.2 (s, CH-*ortho*, B(ArF)<sub>4</sub>, Ar), 129.3 (qq,  $^2J_{\text{CF}} = 31.5$  Hz,  $^4J_{\text{CF}} = 2.7$  Hz, C-CF<sub>3</sub>, B(ArF)<sub>4</sub>), 128.9 (m, ArCH), 125.0 (q,  $^1J_{\text{CF}} = 272.6$  Hz, CF<sub>3</sub>, B(ArF)<sub>4</sub>), 117.9 (sept,  $^3J_{\text{CF}} = 4.0$ , CH-*para*, B(ArF)<sub>4</sub>, Ar), 115.4 (s, ArCH), 113.8 (s, ArCH), 40.7 (s, -N(CH<sub>3</sub>)<sub>2</sub>), 27.4 (vt,  $J_{\text{CP}} = 15.7$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 18.8 (vt,  $J_{\text{CP}} = 2.0$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 17.7 (s, -CH(CH<sub>3</sub>)<sub>2</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  58.2 (s).  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -62.91 (s).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -6.60 (s). IR (NaCl plates)  $\text{cm}^{-1}$ :  $\nu_{\text{CO}}$  2014 (s), 1971 (s). Elemental Anal. Calcd (%) for C<sub>63</sub>H<sub>58</sub>BF<sub>24</sub>IrN<sub>2</sub>O<sub>2</sub>P<sub>2</sub>: C 47.41; H 3.66; N 1.76. Found: C 47.08; H 3.34; N 1.76.

**Synthesis of 3-CO.** To a J. Young Tube charged with 3-Cl (0.034 g, 0.047 mmol) and NaB(ArF)<sub>4</sub> (0.042 g, 0.047 mmol), DCM (0.7 mL) was added. The vessel was degassed and placed under 0.5 atm of CO at room temperature; an immediate colour change from dark green to dark purple was observed. The tube was mixed at room temperature for 1 minute and then degassed. The solution was then filtered and the solvent removed *in vacuo*. Following solvent removal, the purple solid was sonicated in *n*-pentane, filtered and then washed with *n*-pentane (3 × 2 mL). A dark purple solid was obtained in 68% yield (0.050 g, 0.032 mmol). X-Ray quality crystals were obtained from a saturated solution of 3-CO in DCM layered with *n*-pentane that was cooled to -20 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.73 (m, 8H, CH-*ortho*, B(ArF)<sub>4</sub>, Ar), 7.58 (m, 2H, ArH), 7.56 (m, 4H, CH-*para*, B(ArF)<sub>4</sub>, Ar), 6.89 (m, 2H, ArH), 6.83 (dd,  $^4J_{\text{HH}} = 2.4$  Hz,  $^3J_{\text{HH}} = 9.2$  Hz, 2H, ArH), 3.15 (s, 12H, -N(CH<sub>3</sub>)<sub>2</sub>), 2.74 (m, 4H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.17 (m, 24H, -CH(CH<sub>3</sub>)<sub>2</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  260.4 (t,  $^2J_{\text{CP}} = 4.3$  Hz, Ir=C), 195.9 (t,  $^2J_{\text{CP}} = 7.6$  Hz, Ir-CO), 162.1 (q,  $^1J_{\text{CB}} = 49.8$  Hz, C-B, B(ArF)<sub>4</sub>, Ar), 155.7 (vt,  $J_{\text{CP}} = 4.0$  Hz, ArC), 151.2 (vt,  $J_{\text{CP}} = 19.1$  Hz, ArC), 150.0 (vt,  $J_{\text{CP}} = 15.7$  Hz, ArC), 135.2 (s, CH-*ortho*, B(ArF)<sub>4</sub>, Ar), 134.0 (vt,  $J_{\text{CP}} = 6.6$  Hz, ArCH), 129.3 (qq,  $^2J_{\text{CF}} = 31.5$  Hz,  $^4J_{\text{CF}} = 2.7$  Hz, C-CF<sub>3</sub>, B(ArF)<sub>4</sub>), 124.9 (q,  $^1J_{\text{CF}} = 272.4$  Hz, CF<sub>3</sub>, B(ArF)<sub>4</sub>), 117.9 (sept,  $^3J_{\text{CF}} = 4.0$ , CH-*para*, B(ArF)<sub>4</sub>, Ar), 115.3 (s, ArCH), 115.2 (s, ArCH), 41.1 (s, -N(CH<sub>3</sub>)<sub>2</sub>), 26.4 (vt,  $J_{\text{CP}} = 14.9$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 19.5 (vt,  $J_{\text{CP}} = 2.0$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 19.0 (s, -CH(CH<sub>3</sub>)<sub>2</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR (203 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  72.2 (s).  $^{19}\text{F}\{^1\text{H}\}$  NMR (471 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -63.84 (s).  $^{11}\text{B}\{^1\text{H}\}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -6.04 (s). IR (NaCl plates)  $\text{cm}^{-1}$ :  $\nu_{\text{CO}}$  1963 (s). Elemental Anal. Calcd (%) for C<sub>62</sub>H<sub>58</sub>BF<sub>24</sub>IrN<sub>2</sub>O<sub>2</sub>P<sub>2</sub>: C 47.49; H 3.73; N 1.79. Found: C 47.44; H 3.94; N 1.95.

**Synthesis of 4-(CO)<sub>2</sub>.** Complex 4-Cl (0.008 g, 0.011 mmol) and NaB(ArF)<sub>4</sub> (0.014 g, 0.016 mmol) were dissolved together in  $\text{CD}_2\text{Cl}_2$  (0.7 mL) in a J. Young NMR tube. The mixture was



degassed, placed under 1 atm CO gas and allowed to mix at room temperature for ten minutes. An immediate colour change from dark brown to deep green was observed. The volatiles were then removed *in vacuo* and the green product was filtered through Celite followed by recrystallization from a CH<sub>2</sub>Cl<sub>2</sub>/pentane solution. Compound **4-(CO)<sub>2</sub>** was isolated as a dark green crystalline solid in 85% yield (0.015 g, 0.009 mmol). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.06 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2H, ArH), 7.91 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2H, ArH), 7.78 (t, <sup>3</sup>J<sub>HH</sub> = 8.3 Hz, 2H, ArH), 7.72 (s br, 8H, CH-*ortho* B(ArF)<sub>4</sub>, Ar), 7.56 (s br, 4H, CH-*para* B(ArF)<sub>4</sub>, Ar), 7.54 (t, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 2H, ArH), 3.20 (septvt, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, J<sub>HP</sub> = 1.9 Hz, 4H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.39 (dvt, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, J<sub>HP</sub> = 8.1 Hz, 12H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.21 (dvt, <sup>3</sup>J<sub>HH</sub> = 7.2, J<sub>HP</sub> = 7.0 Hz, 12H, -CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 200.1 (t, <sup>2</sup>J<sub>CP</sub> = 4.9 Hz, Ir-CO), 182.1 (t, <sup>2</sup>J<sub>CP</sub> = 5.5 Hz, C=Ir), 175.6 (vt, J<sub>CP</sub> = 20.8 Hz, ArC), 162.1 (q, <sup>1</sup>J<sub>CB</sub> = 49.7 Hz, C-B B(ArF)<sub>4</sub>, Ar), 147.5 (vt, J<sub>CP</sub> = 5.0 Hz, ArC), 138.8 (vt, J<sub>CP</sub> = 3.4 Hz, ArC), 138.3 (vt, J<sub>CP</sub> = 23.9 Hz, ArC), 135.2 (s, CH-*ortho*, B(ArF)<sub>4</sub>, Ar) 129.2 (qq, <sup>2</sup>J<sub>CF</sub> = 31.5 Hz, <sup>4</sup>J<sub>CF</sub> = 3.0 Hz, C-CF<sub>3</sub> B(ArF)<sub>4</sub>), 128.1 (s, ArCH), 127.9 (s, ArCH), 126.1 (s, ArCH), 125.0 (q, <sup>1</sup>J<sub>CF</sub> = 272.3 Hz, CF<sub>3</sub> B(ArF)<sub>4</sub>), 123.5 (s, ArCH), 117.9 (sept, <sup>3</sup>J<sub>CF</sub> = 4.0 Hz, CH-*para*, B(ArF)<sub>4</sub>, Ar), 27.9 (vt, J<sub>CP</sub> = 15.4 Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 20.3 (s, -CH(CH<sub>3</sub>)<sub>2</sub>), 18.5 (s, -CH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (203 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 47.1 (s). <sup>19</sup>F NMR (471 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -63.8 (s). <sup>11</sup>B{<sup>1</sup>H} NMR (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -6.0 (s). IR (NaCl) cm<sup>-1</sup>: 2014 (s), 2055 (s). Elemental Anal. Calcd (%) for C<sub>63</sub>H<sub>48</sub>B<sub>24</sub>IrO<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: C 46.65; H 2.98. Found: C 46.52; H 2.99.

**Synthesis of 4-CO.** Compound **4-(CO)<sub>2</sub>** was dissolved in CH<sub>2</sub>Cl<sub>2</sub> in a J. Young NMR tube. The solvent was removed *in vacuo* and the residue was heated with a heat gun until a colour change from green to pink-red was observed. This process was repeated 3–4 times until full conversion was achieved, as monitored by <sup>31</sup>P NMR spectroscopy. An alternative method was also employed whereby **4-Cl** (10 mg, 0.014 mmol) was dissolved in 0.7 mL CH<sub>2</sub>Cl<sub>2</sub> in a J. Young NMR tube. The solution was degassed followed by the addition of *ca.* 0.5 atm CO gas. The tube was shaken during which a rapid colour change from dark brown to dark turquoise was observed. Almost immediately after addition of CO, the sample was pumped to dryness removing any excess CO. NaB(ArF)<sub>4</sub> (12 mg, 0.014 mmol) was added to the J. Young tube and the mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, resulting in a deep pink solution. The solution was filtered through Celite and the volatiles were removed *in vacuo*. Compound **4-CO** was isolated as a dark pink solid in 93% yield (20 mg, 0.013 mmol). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.39 (d, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 2H, ArH), 8.09 (t, J = 8.2 Hz, 2H, ArH), 7.88 (d, J = 8.3 Hz, 2H, ArH), 7.72 (s br, 8H, CH-*ortho* B(ArF)<sub>4</sub>, Ar), 7.56 (t, J = 7.7 Hz, 2H, ArH), 7.55 (s br, 4H, CH-*para*, B(ArF)<sub>4</sub>, Ar), 3.28 (m, 4H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.45 (dvt, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, J<sub>HP</sub> = 7.7 Hz, 12H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (dvt, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, J<sub>HP</sub> = 8.0 Hz, 12H, -CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 232.2 (C=Ir), 188.6 (t, <sup>2</sup>J<sub>CP</sub> = 7.8 Hz, Ir-CO), 173.1 (vt, J<sub>CP</sub> = 19.2 Hz, ArC), 162.1 (q, <sup>1</sup>J<sub>CB</sub> = 49.7 Hz, C-B B(ArF)<sub>4</sub>, Ar), 161.4 (vt, J<sub>CP</sub> = 16.4 Hz, ArC), 153.9 (vt, J<sub>CP</sub> = 4.2 Hz, ArC), 139.4 (vt, J<sub>CP</sub> = 1.7 Hz, ArC), 135.2 (s, CH-*ortho*

B(ArF)<sub>4</sub>), 132.8 (s, ArCH), 129.2 (qq, <sup>2</sup>J<sub>CF</sub> = 31.5 Hz, <sup>4</sup>J<sub>CF</sub> = 3.0 Hz, C-CF<sub>3</sub> B(ArF)<sub>4</sub>), 129.2 (s, ArCH), 127.2 (s, ArCH), 127.0 (s, ArCH), 125.0 (q, <sup>1</sup>J<sub>CF</sub> = 272.3 Hz, CF<sub>3</sub> B(ArF)<sub>4</sub>), 117.9 (sept, <sup>3</sup>J<sub>CF</sub> = 4.0 Hz, CH-*para*, B(ArF)<sub>4</sub>, Ar), 27.4 (vt, J<sub>CP</sub> = 15.4 Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 20.8 (vt, J<sub>CP</sub> = 2.7 Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 20.7 (s, -CH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (203 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 59.6 (s). <sup>19</sup>F{<sup>1</sup>H} NMR (471 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -63.8 (s). <sup>11</sup>B{<sup>1</sup>H} NMR (161 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -6.0 (s). IR (NaCl) cm<sup>-1</sup>: ν<sub>CO</sub> 2048 (s). HRMS (APCI) for C<sub>30</sub>H<sub>36</sub>IrOP<sub>2</sub>S<sub>2</sub>; calculated (M<sup>+</sup>): 731.1312 (100%); found (M<sup>+</sup>): 731.1331 (100%).

**Synthesis of 5-(CO)<sub>2</sub>.** To a thick walled glass pressure flask (25 mL) charged with **5-Cl** (0.030 g, 0.037 mmol), NaB(ArF)<sub>4</sub> (0.033 g, 0.037 mmol) and a Teflon stirbar, DCM (5 mL) was vacuum transferred at -78 °C. Following vacuum transfer, the mixture was warmed to room temperature and the atmosphere was replaced with CO (1 atm) which resulted in an immediate colour change from dark brownish-green to dark red. The solution was stirred for 5 minutes, at which point the solution was filtered. The solvent was removed *in vacuo* from the red filtrate and a red solid was obtained in 99% yield (0.062 g, 0.037 mmol). If the isolated material was found to be a mixture of **5-CO** and **5-(CO)<sub>2</sub>** the obtained solid could be placed under an atmosphere of CO to obtain pure compound. The desired compound was also obtained in quantitative yield by exposing **5-CO** dissolved in DCM to an atmosphere of CO. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.72 (br m, 8H, CH-*ortho*, B(ArF)<sub>4</sub>, Ar), 7.55 (s, 4H, CH-*para*, B(ArF)<sub>4</sub>, Ar), 6.99 (m, 2H, ArH), 6.71 (d, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 2H, ArH), 3.48 (br m, 8H, -N(CH<sub>2</sub>)<sub>5</sub>), 2.75 (m, 4H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.73 (br m, 12H, -N(CH<sub>2</sub>)<sub>5</sub>), 1.17 (m, 24H, -CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 207.4 (t, <sup>2</sup>J<sub>CP</sub> = 5.2 Hz, Ir=C) 178.2 (t, <sup>2</sup>J<sub>CP</sub> = 5.7 Hz, Ir-CO), 162.3 (q, <sup>1</sup>J<sub>CB</sub> = 49.8 Hz, C-B, B(ArF)<sub>4</sub>, Ar), 156.2 (vt, <sup>3</sup>J<sub>CP</sub> = 5.1 Hz, C-N(CH<sub>2</sub>)<sub>5</sub>, ArC), 150.8 (vt, J<sub>CP</sub> = 9.5 Hz, C-O, ArC), 143.9 (vt, J<sub>CP</sub> = 23.5 Hz, C-P(<sup>i</sup>Pr)<sub>2</sub>, ArC), 136.4 (vt, J<sub>CP</sub> = 18.3 Hz, ArC), 135.3 (s, CH-*ortho*, B(ArF)<sub>4</sub>, Ar), 129.4 (qq, <sup>2</sup>J<sub>CF</sub> = 31.4 Hz, <sup>4</sup>J<sub>CF</sub> = 2.7 Hz, C-CF<sub>3</sub>, B(ArF)<sub>4</sub>), 125.1 (q, <sup>1</sup>J<sub>CF</sub> = 272.5 Hz, CF<sub>3</sub>, B(ArF)<sub>4</sub>), 118.0 (sept, <sup>3</sup>J<sub>CF</sub> = 3.8 Hz, CH-*para*, B(ArF)<sub>4</sub>, Ar), 116.2 (s, ArCH), 101.8 (s, ArCH), 49.5 (s, -N(CH<sub>2</sub>)<sub>5</sub>), 27.9 (vt, J<sub>CP</sub> = 15.6 Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 25.7 (s, -N(CH<sub>2</sub>)<sub>5</sub>), 24.5 (s, -N(CH<sub>2</sub>)<sub>5</sub>), 18.9 (s, -CH(CH<sub>3</sub>)<sub>2</sub>), 17.6 (s, -CH(CH<sub>3</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (203 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 65.8 (s). <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -62.9 (s). <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -6.57 (s). IR (NaCl plates) cm<sup>-1</sup>: ν<sub>CO</sub> 2014 (s), 1973 (s). Repeated attempts to obtain satisfactory elemental analyses met with failure for this sample.

**Synthesis of 5-CO.** Compound **5-Cl** (0.023 g, 0.029 mmol), NaB(ArF)<sub>4</sub> (0.026 g, 0.029 mmol) and DCM (0.7 mL) were added to a J. Young NMR tube. The vessel was degassed, placed under 0.75 atm of CO at room temperature and mixed for 1 minute. Following the addition of CO an immediate colour change from dark brown to a dark pinkish-red was observed. The tube was then degassed and the solution filtered. Solvent was removed *in vacuo* and the solid was left under high vacuum for 4 hours. A red solid was obtained in 76% yield (0.036 g, 0.022 mmol). Compound **5-CO** could also be prepared with the heating method used to make **iPr-2-CO**



but at a reduced temperature of 80 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.73 (m, 8H, CH-*ortho*, B(Ar<sup>F</sup>)<sub>4</sub>, Ar), 7.56 (s, 4H, CH-*para*, B(Ar<sup>F</sup>)<sub>4</sub>, Ar), 7.16 (m, 2H, ArH), 6.82 (d,  $^3J_{\text{HH}} = 1.9$  Hz, 2H, ArH), 3.60 (br m, 8H, -N(CH<sub>2</sub>)<sub>5</sub>), 2.80 (m, 4H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.76 (m, 12H, -N(CH<sub>2</sub>)<sub>5</sub>), 1.26 (dvt,  $^3J_{\text{HH}} = 10.1$  Hz,  $J_{\text{HP}} = 7.3$  Hz, 12H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.14 (dvt,  $^3J_{\text{HH}} = 8.6$  Hz,  $J_{\text{HP}} = 7.1$  Hz, 12H, -CH(CH<sub>3</sub>)<sub>2</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  214.9 (t,  $^2J_{\text{CP}} = 5.0$  Hz, Ir=C), 196.4 (t,  $^2J_{\text{CP}} = 6.6$  Hz, Ir-CO), 162.2 (q,  $^1J_{\text{CB}} = 49.7$  Hz, C-B, B(Ar<sup>F</sup>)<sub>4</sub>, Ar), 157.8 (vt,  $J_{\text{CP}} = 4.5$  Hz, C-N(CH<sub>2</sub>)<sub>5</sub>, ArC), 154.5 (vt,  $J_{\text{CP}} = 8.9$  Hz, C-O, ArC), 149.5 (vt,  $J_{\text{CP}} = 19.7$  Hz, C-P(<sup>t</sup>Pr)<sub>2</sub>, ArC), 136.9 (vt,  $J_{\text{CP}} = 19.4$  Hz, ArC), 135.3 (s, CH-*ortho*, B(Ar<sup>F</sup>)<sub>4</sub>, Ar), 129.4 (qq,  $^2J_{\text{CF}} = 31.5$  Hz,  $^4J_{\text{CF}} = 2.6$  Hz, C-CF<sub>3</sub>, B(Ar<sup>F</sup>)<sub>4</sub>), 125.1 (q,  $^1J_{\text{CF}} = 273.0$  Hz, CF<sub>3</sub>, B(Ar<sup>F</sup>)<sub>4</sub>), 117.9 (sept,  $^3J_{\text{CF}} = 4.1$  Hz, CH-*para*, B(Ar<sup>F</sup>)<sub>4</sub>, Ar), 116.2 (s, ArCH), 100.0 (s, ArCH), 49.6 (s, -N(CH<sub>2</sub>)<sub>5</sub>), 27.7 (vt,  $J_{\text{CP}} = 14.4$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 25.9 (s, -N(CH<sub>2</sub>)<sub>5</sub>), 24.4 (s, -N(CH<sub>2</sub>)<sub>5</sub>), 19.9 (vt,  $^2J = 2.4$  Hz, -CH(CH<sub>3</sub>)<sub>2</sub>), 19.4 (s, -CH(CH<sub>3</sub>)<sub>2</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR (203 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  78.6 (s).  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -62.9 (s).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -6.58 (s). IR (NaCl plates)  $\text{cm}^{-1}$ :  $\nu_{\text{CO}}$  1974 (s). Elemental Anal. Calcd (%) for C<sub>68</sub>H<sub>64</sub>BF<sub>24</sub>IrN<sub>2</sub>O<sub>2</sub>P<sub>2</sub>: C 49.14; H 3.88; N 1.69. Found: C 49.04; H 4.19; N 1.61.

**Synthesis of 6-Cl.** Compound 1-Cl (0.020 g, 0.034 mmol) was dissolved with  $\text{CD}_2\text{Cl}_2$  (0.5 mL) in a J. Young NMR tube. The solution was then degassed and placed under 1 atm of CO at room temperature. Upon addition of CO, the dark green solution turned pale yellow. All volatiles were removed *in vacuo* and the product was isolated as a pale yellow solid in 92% yield (0.018 g, 0.030 mmol). X-ray quality crystals were obtained from a  $\text{CD}_2\text{Cl}_2$  solution layered with pentane.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.04 (d,  $^3J_{\text{HH}} = 8.1$  Hz, 2H, ArH), 7.80 (dvt,  $^3J_{\text{HH}} = 6.9$  Hz,  $J_{\text{HP}} = 3.4$  Hz, 2H, ArH), 7.43 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2H, ArH), 7.28 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2H, ArH), 1.52 (vt,  $J_{\text{HP}} = 7.2$  Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.4 (vt,  $J_{\text{HH}} = 6.7$  Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  212.3 (dt,  $^1J_{\text{CRh}} = 26.5$  Hz,  $^2J_{\text{CP}} = 5.8$  Hz, CO) Hz, 151.1 (vt,  $J_{\text{CP}} = 12.2$  Hz, ArC), 134.6 (s, ArCH), 130.8 (dvt,  $J_{\text{CP}} = 14.5$  Hz,  $J_{\text{CRh}} = 2.3$  Hz ArC), 129.7 (s, ArCH), 126.7 (vt,  $J_{\text{CP}} = 4.6$  Hz, ArCH), 124.4 (vt,  $J_{\text{CP}} = 3.0$  Hz, ArCH), 39.2 (vt,  $J_{\text{CP}} = 6.8$  Hz, -C(CH<sub>3</sub>)<sub>3</sub>), 38.0 (vt,  $J_{\text{CP}} = 8.4$  Hz, -C(CH<sub>3</sub>)<sub>3</sub>), 30.9 (vt,  $J_{\text{CP}} = 3.0$  Hz, -C(CH<sub>3</sub>)<sub>3</sub>), 30.1 (vt,  $J_{\text{CP}} = 3.0$  Hz, -C(CH<sub>3</sub>)<sub>3</sub>), 23.6 (dt,  $^1J_{\text{CRh}} = 11.1$  Hz,  $^2J_{\text{CP}} = 4.0$  Hz, RhC).  $^{31}\text{P}\{^1\text{H}\}$  NMR (243 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  60.6 (d,  $^1J_{\text{PRh}} = 123.6$  Hz). IR (NaCl plates)  $\text{cm}^{-1}$ :  $\nu_{\text{CO}}$  1787 (s). Elemental Anal. Calcd (%) for C<sub>30</sub>H<sub>46</sub>ClO<sub>2</sub>P<sub>2</sub>Rh: C 58.03, H 7.14; Found: C 57.89, H 7.33.

**Synthesis of 6-CO.** To a thick walled glass pressure flask (25 mL) charged with 1-Cl (0.038 g, 0.064 mmol) and NaB(Ar<sup>F</sup>)<sub>4</sub> (0.057 g, 0.064 mmol), DCM (5 mL) was added *via* vacuum transfer at -78 °C. Following vacuum transfer, the atmosphere was replaced with CO (1 atm), which resulted in an immediate color change of the solution from green to dark yellow. The solution was stirred for 1 hour, at which point the reaction was filtered. The filtrate was collected and solvent was removed *in vacuo*. A dark yellow solid was isolated in 73% yield (0.067 g, 0.045 mmol). Complex 6-CO was also synthesized quantitatively at room temperature by placing a solution of 1-CO in DCM under 1 atm of CO, mixing for 10 minutes and

removing volatiles *in vacuo*. X-ray quality crystals were obtained from a  $\text{CD}_2\text{Cl}_2$  solution layered with pentane.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.09 (d,  $^3J_{\text{HH}} = 7.8$  Hz, 2H, ArH), 7.94 (m, ArH), 7.78 (m, 8H, B(Ar<sup>F</sup>)<sub>4</sub>, ArH), 7.68 (t,  $^3J_{\text{HH}} = 7.4$  Hz, 2H, ArH), 7.60 (s, 4H, B(Ar<sup>F</sup>)<sub>4</sub>, ArH), 7.51 (d,  $^3J_{\text{HH}} = 7.0$  Hz, 2H, ArH), 1.50 (vt,  $J_{\text{CP}} = 7.7$  Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.32 (vt,  $J_{\text{CP}} = 7.7$  Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  195.3 (dt,  $^1J_{\text{CRh}} = 22.1$  Hz,  $^2J_{\text{CP}} = 5.3$  Hz, Rh(CO)C), 190.1 (dt,  $^1J_{\text{CRh}} = 66$  Hz,  $^2J_{\text{CP}} = 12.4$  Hz, Rh-CO), 162.3 (q,  $J_{\text{CB}} = 50.2$  Hz, C-B B(Ar<sup>F</sup>)<sub>4</sub>, Ar), 146.4 (vt,  $J_{\text{CP}} = 12.6$  Hz, ArC) 135.3 (m, B(Ar<sup>F</sup>)<sub>4</sub>, ArCH), 135.3 (s, ArCH), 133.0 (s, ArCH), 129.6 (vt,  $J_{\text{CP}} = 18.0$  Hz, ArC) 129.4 (qq,  $^2J_{\text{CF}} = 31.3$  Hz,  $^4J_{\text{CF}} = 2.9$  Hz, B(Ar<sup>F</sup>)<sub>4</sub>, ArC-CF<sub>3</sub>), 128.4 (vt,  $J_{\text{CP}} = 6.8$  Hz, ArCH), 127.8 (vt,  $J_{\text{CP}} = 3.6$  Hz, ArCH), 125.1 (q,  $J_{\text{CF}} = 272.4$  Hz, B(Ar<sup>F</sup>)<sub>4</sub>, CF<sub>3</sub>), 118.0 (sept,  $J_{\text{CF}} = 4.4$  Hz, B(Ar<sup>F</sup>)<sub>4</sub>, ArCH), 44.3 (dt,  $^1J_{\text{CRh}} = 6.7$  Hz,  $^2J_{\text{CP}} = 3.5$  Hz, Rh-(CO)C) 40.5 (vt,  $J_{\text{CP}} = 8.7$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 39.8 (vt,  $J_{\text{CP}} = 9.7$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 30.9 (m, C(CH<sub>3</sub>)<sub>3</sub>), 30.8 (m, C(CH<sub>3</sub>)<sub>3</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR (203 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  79.0 (d,  $J_{\text{PRh}} = 106.8$  Hz).  $^{19}\text{F}$  NMR (471 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -63.8.  $^{11}\text{B}\{^1\text{H}\}$  NMR (161 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -6.0. IR (NaCl plates)  $\text{cm}^{-1}$ :  $\nu_{\text{CO}}$  2050 (s), 1860 (m). Elemental Anal. Calcd (%) for C<sub>63</sub>H<sub>56</sub>BF<sub>24</sub>O<sub>2</sub>P<sub>2</sub>Rh: C 51.24, H 3.82; Found: C 50.85, H 3.66.

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